

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification<sup>6</sup> :</b> <b>C08L 63/00, 77/06, 97/02, C08K 3/20</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 95/27008</b> <b>(43) International Publication Date:</b> 12 October 1995 (12.10.95)
<b>(21) International Application Number:</b> PCT/US95/03769 <b>(22) International Filing Date:</b> 28 March 1995 (28.03.95)  <b>(30) Priority Data:</b> 08/221,296      31 March 1994 (31.03.94)      US  <b>(71) Applicant:</b> HENKEL CORPORATION [US/US]; Suite 150, 140 Germantown Pike, Plymouth Meeting, PA 19462 (US).  <b>(72) Inventors:</b> CLUNGEON, Nancy, S.; Apartment 1811, 1908 Paces Landing Avenue, Rock Hill, SC 29732 (US). DE- VORE, David, I.; 112 Alberts Way, Langhorne, PA 19047 (US). FISCHER, Stephen, A.; 307 Anderson Road, Yard- ley, PA 19067 (US). GIORDAN, Judith, C.; 520 Spring Mill, Road, Villanova, PA 19085 (US).  <b>(74) Agent:</b> GRANDMAISON, Real, J.; Henkel Corporation, Suite 150, 140 Germantown Pike, Plymouth Meeting, PA 19462 (US).		<b>(81) Designated States:</b> CA, FI, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> WET STRENGTH RESIN COMPOSITION AND METHODS OF MAKING THE SAME  <b>(57) Abstract</b>  Wet-strength resins and methods of making the same by reacting a polyamine, polyaminoamide or alkylated derivative thereof with a cross-linking agent selected from diepoxides, piperazine dichlorohydrin, methylene bis-acrylamide, chloroacetyl chloride and maleic anhydride.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

WET STRENGTH RESIN COMPOSITION  
AND METHODS OF MAKING THE SAME

BACKGROUND OF THE INVENTION

1.0 Field Of The Invention:

5           The present invention relates to wet strength resin compositions and methods of making the same and particularly to improved wet strength resins which eliminate the generation of 1,3-dichloro-2-propanol, epichlorohydrin and 1-chloro-2,3-propanediol.

10          2. Description Of Related Art:

          Polyamine-epichlorohydrin resins have been used as wet strength resins for paper since the early 1950's. Such resins are cationic and are particularly useful because they are formaldehyde-free and develop wet strength at  
15       neutral or alkaline pH values.

          One of the drawbacks associated with the use of polyamine-epichlorohydrin resins is the emission of harmful chlorinated compounds into the water systems of pulp and paper mills. These chlorinated compounds, including 1,3  
20       dichloro-2- propanol, epichlorohydrin and 1-chloro-2,3-propanediol, are usually discharged into the effluent waste water systems because they are only partially substantive to cellulose pulp fibers. The permissible amounts of these

chlorinated compounds are decreasing and therefore efforts have been made to reduce the amounts of these materials.

Fischer et al, U.S. Patent No. 5,116, 887; European Patent Publication No. 0 508 203; Devore et al., U.S. Patent Nos. 5,189,142 and 5,239,047; and Fischer et al., U.S. Serial No. 08/165,779 filed December 10, 1993 disclose efforts at modifying the conditions under which polyamine-epichlorohydrin resins are prepared to reduce the amount of volatile organic compounds.

It would be of significant advance in the art of making paper to employ wet strength resins which are derived from cross-linking agents other than epichlorohydrin to eliminate the generation of such chlorinated by-products and yet possess excellent wet-strength properties.

### 3.0 Summary of the Invention

The present invention is directed to wet-strength resins which are cationic and thermosetting, and to methods of producing the same which eliminate the generation of the by-products 1,3-dichloro-2-propanol, epichlorohydrin and 1-chloro-2,3-propanediol.

The wet strength resins are produced by reacting an amine compound including a polyamine sharing at least two reactive amine sites, polyaminoamides and alkylated polyaminoamides with a cross-linking agent selected from the group consisting of diepoxides, piperazine dichlorohydrin, methylene bis-acrylamide, chloroacetyl

chloride and maleic anhydride. The cross-linking agents employed in the wet strength resins of the present invention are present in an amount sufficient to provide a mole ratio with reactive nitrogen of the amine compound of at least about 0.375, preferably from about 0.375 to about 3.0. The resulting wet-strength resins eliminate the generation of the above-mentioned by-products and have excellent wet-strength properties.

10

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention is premised on the discovery that wet strength resins using select cross-linking agents in particular amounts can be produced which eliminate the generation of 1,3-dichloro-2-propanol, epichlorohydrin and 1-chloro-2,3-propanediol. In addition, the resulting resins exhibit good wet strength properties, comparable to those resins made with epichlorohydrin, as determined by measuring the strength of paper sheets made with the resins of the present invention.

20

The cross-linking agents employed in the present invention include diepoxides such as 5-ethyl-1,3-diglycidyl-5-methyl hydantoin, dimethyl hydantoin diepoxide, pentamethylene hydantoin diepoxide, ethyl amyl diepoxide, and 1,4-butane diepoxide; piperazine dichlorohydrin; methylene bis-acrylamide; chloroacetyl chloride; and maleic anhydride. These cross-linking agents have been used to cross-link polyamines and polyaminoamides to produce cosmetic compositions for the conditioning of

hair as disclosed in Vanlerberghe et al., U.S. Patent No. 4,277,581. The cross-linking agent for hair conditioning is employed in a mole ratio with reactive nitrogen of the amine compound of from 0.025 to 0.35.

5 Applicants have discovered that resin compositions using some of the same cross-linking agents but in greater mole ratios of at least 0.375 mole per mole of reactive nitrogen of the amine compound, provide excellent wet-strength properties to paper.

10 Wet-strength resins of the present invention of the polyamine type are prepared by reacting a polyamine and the cross-linking agent in an aqueous polyol solution.

A polyamine is any amine that has at least two amine functionalities such as a simple diamine (e.g. ethylene diamine) or more than two amine functionalities such as diethylene triamine, triethylene tetramine, tetraethylene pentamine, bis-hexamethylene triamine, polyethyleneimine, polyallylamine, and polydiallylamine, and the like. Preferably, the polyamine is a mixture of polyamines known as amine still bottoms which is a mixture of polyamines containing from about 35% to 70% by weight bis-hexamethylenetriamine. It has been found that at least one polyol is a necessary component of the reaction because it performs the dual function of a co-solvent and a moderator of the cross-linking reaction.

15  
20  
25

The polyol component of the wet strength resin composition can be any aliphatic compound having two or more hydroxyl functionalities that is miscible with water

or combinations thereof. Examples of such polyols include ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, 1,6-hexylene glycol, glycerol, monosaccharides such as glucose or fructose, disaccharides such as sucrose, and polyvinyl alcohol. The preferred polyols are 1,2-propylene glycol and dipropylene glycol because they are generally recognized as safe, have flash points  $>200^{\circ}\text{C}$ , and are good co-solvents for the polyamine-cross-linking agent reaction.

The process of the present invention is conducted generally by adding the cross-linking agent to a water-polyol-polyamine solution at a rate sufficient to maintain the temperature of the solution in a range of from about  $5^{\circ}\text{C}$  to  $25^{\circ}\text{C}$  to form a reaction mixture having a mole ratio of the cross-linking agent to the reactive nitrogen of the amine compound of about at least 0.375, preferably from about 0.375 to 3.0. The temperature of the reaction in accordance with the present invention is no higher than  $100^{\circ}\text{C}$ , preferably in the range of from 15 to  $50^{\circ}\text{C}$ .

Wet strength resins of the present invention may also be prepared by reacting a solution of a polyaminoamide or alkylated derivative thereof with the cross-linking agent. The polyaminoamide is prepared by reacting a diacid such as glutaric acid, adipic acid, mixtures thereof and/or diesters such as dimethyl glutarate, dimethyl adipate and mixtures thereof with one of the amine compounds (e.g. diethyl triamine) mentioned above for preparing the polyamine. The cross-linking agent is added to a

polyaminoamide aqueous solution at a rate sufficient to maintain the temperature of the solution from about 5°C to 50°C to form a reaction mixture having a mole ratio of the cross-linking agent to the reactive nitrogen of the amine compound of at least about 0.375, preferably from about 0.375 to about 3.0. The cross-linking reaction is carried out at a temperature of from about 15 to 100°C.

#### EXAMPLE 1

##### Preparation of a Polyaminoamide Resin

269 g of dibasic acid ester mixture comprised of 65% dimethyl glutarate and 35% dimethyl adipate and 170 g of diethylene triamine was charged to a resin reactor. Stirring and nitrogen sparge were started and the contents of the reactor were heated to 150°C. The temperature was maintained until the start of a methanol reflux. The reflux temperature was allowed to continue until the reaction temperature dropped to 85°C, at which time the methanol was distilled off from the product, allowing the reaction temperature to rise to 150°C during the distillation process which produced 109 g of methanol. A 32.9% solids content polyaminoamide resin solution was made by dissolving the reaction product in 670 g of water. The total alkalinity was 274.8 mg KOH/g dry resin.

#### EXAMPLE 2

##### Preparation of an Alkylated Polyaminoamide Resin



297.6 g of the polyaminoamide resin prepared by the method described in Example 1, having a solids content of 50.4% and a total alkalinity of 277.2 mg KOH/g dry resin, and 196.4 g of deionized water were charged to a pressure reactor. Stirring and nitrogen sparge were started and the contents of the reactor were heated to about 80°C. The nitrogen was discontinued and the reactor was pressurized to 40 psi with methyl chloride gas. The reaction conditions were maintained until the total alkalinity reached zero. The alkylated polyaminoamide solution was adjusted to a pH of 10 with 37.5 g of a 50% aqueous NaOH solution. The resin solids content was 39.7% and contained 1.77% by weight of tertiary amine based on the total weight of the solution determined by titration.

## EXAMPLE 3

Reaction of Alkylated Polyaminoamide with Diepoxide

115.5 g of the alkylated polyaminoamide produced in accordance with Example 2, having 1.77% by weight of a tertiary amine and a 39.7% solids content, 49.7 g of deionized water, and 29.5 g of 5-ethyl-1,3-diglycidyl-5-methyl hydantoin, having 11.9% by weight of epoxide groups as determined by titration, were charged to a round bottom reaction flask. The contents of the reactor were mixed at 25°C until the solution viscosity reached about 265 cps as measured on a Brookfield viscometer using spindle 2, 60 rpm at 25°C. About 257.1 g of deionized water was added to dilute the reaction solution to about 15% resin solids content and stirring continued until the viscosity reached 45 cps (Brookfield viscometer, spindle 2, 60 rpm at 25°C), at which time the pH of the reaction solution was adjusted to 2.0 with 13.8 g of 37% hydrochloric acid. The final resin solution contained a 16.8% solids content, and had a pH of 2.0, and a Brookfield viscosity of 41 cps at 25°C.

20

## EXAMPLE 4

Preparation of Piperazine Dichlorohydrin

40 g of piperazine and 117.4 g of deionized water were charged to a round bottom reaction flask. The mixture was heated to about 35°C until all of the piperazine was dissolved. The solution was cooled to about 30°C and epichlorohydrin was added at a controlled rate sufficient to maintain a reaction temperature of about 30-40°C. The

reaction temperature was maintained for 6 hours and then cooled and discharged. The solids content of the solution was 50.4% with a pH of 6.1 and a total alkalinity and free epoxide content of zero.

5

**EXAMPLE 5**Reaction of Polyaminoamide with Piperazine Dichlorohydrin

103.4 g of polyaminoamide prepared by the method described in Example 1, having a solids content of 48.3% and a total alkalinity of 289.29 mg KOH/g dry resin, 8.8 g of deionized water, and 52.6 g of piperazine dichlorohydrin produced in accordance with Example 4, was charged to a round bottom reaction flask. The mixture was heated to about 30°C until the Brookfield viscosity of the solution reached about 1100 cps (spindle 3, 30 rpm at 25°C). Deionized water (362.8 g) was added to the reaction flask and the reaction was continued at 30°C until the Brookfield viscosity reached about 60.0 cps (spindle 2, 60 rpm at 25°C), at which time the pH of the aqueous solution was adjusted to 3.0 using 21.5 g of 37% hydrochloric acid. The Brookfield viscosity of the resin was about 67.5 cps (spindle 2, 60 rpm at 25°C) and the solids content was 14.5%.

**EXAMPLE 6**Reaction of Polyaminoamide with Methylene bis-Acrylamide

110.0 g of the polyaminoamide resin prepared by the method described in Example 1, having a solids content of

48.6% and a total alkalinity of 282 mg KOH/g dry resin, 173.2 g of deionized water, 1.4 g of a 50% aqueous solution of NaOH, and 4.5 g of glycidyl trimethylammonium chloride was charged to a round bottom reaction flask. The reactor contents were heated to 85°C for 3.5 hours and then cooled to 25°C where 18.7 g methylene bis-acrylamide was added and reacted at about 50°C until the reaction mass gelled. 292.1 g of deionized water and 13 g of 37% hydrochloric acid were rapidly added. The resulting resin had a pH of 1.0, a Brookfield viscosity of 165 cps (spindle 2, 60 rpm at 25°C), and a solids content of 10.3%.

#### EXAMPLE 7

##### Reaction of Polyaminoamide with Chloroacetyl Chloride

125.3 g of the polyaminoamide resin prepared by the method described in Example 1, having a solids content of 48.8% and a total alkalinity of 283 mg KOH/g dry resin, 62.7 g of deionized water, and 5.1 g glycidyl trimethylammonium chloride were charged to a round bottom reaction flask. The reactor contents were heated to 85°C for 2.0 hours and cooled to 25°C where 17.5 g of a 50% aqueous solution of NaOH was added. The reactor contents were cooled to 10°C and 23.6 g chloroacetyl chloride was added at a rate sufficient to control the reaction temperature below 20°C. The reaction contents were heated to 32°C and 313.3 g of deionized water and 9.4 g of 37% hydrochloric acid were added after the Brookfield viscosity reached 890 cps (spindle 2, 30 rpm at 25°C). The resulting

resin had a pH of 3.0, a Brookfield viscosity of 45 cps (spindle 2, 60 rpm at 25°C), and a solids content of 15.3%.

As shown in Table 1, Examples 3 and 5, 6 and 7 provided wet strength resins which exhibited excellent wet strength characteristics as compared to paper which was untreated.

#### EXAMPLE 8

##### Reaction of Polyaminoamide with Maleic Anhydride

140.2 g of dibasic acid ester mixture comprised of 65% dimethyl glutarate and 35% dimethyl adipate and 164.3 g of diethylene triamine were charged to a resin reactor. Stirring and nitrogen sparge were started and the contents of the reactor were heated to 150°C. This temperature was maintained until the start of methanol reflux. The reflux temperature was allowed to continue until the reaction temperature dropped to 85°C, at which time the methanol was distilled off from the product allowing the reaction temperature to rise to 150°C during the distillation which produced 157.4 g of methanol. A 51.3% solids content of polyaminoamide resin solution was made by dissolving the reaction product in 337 g of water. The total alkalinity was determined to be 360 mg KOH/g dry resin. Part of the polyaminoamide solution (87.7g) was transferred to a round bottom reaction flask and 72.0 g of deionized water, 0.1 g of a 50% aqueous solution of NaOH, and 6.1 g of 72.5% actives solution of glycidyl trimethylammonium chloride were added and heated to 85°C for 2 hours, after which, the

reactor contents were cooled to 25°C and 12.6 g of maleic anhydride was added. The contents of the reactor were heated to about 70-85°C until the reaction mass gelled and 71.5 g of deionized water was rapidly added. The resulting resin had a pH of 6.4, a Brookfield viscosity of 221 cps (spindle 2, 60 rpm at 25°C), and a solids content of 18.6%.

#### EXAMPLE 9

Commercial bleached kraft stock of about 3% consistency was diluted to 0.2% with water. Blank handsheets were prepared according to the handsheet preparation method outlined in the Mark IV Dynamic Handsheet Mold/Paper Chemistry Jar Assembly operating manual. Treated handsheets were prepared by the same method except the wet strength resin of the present invention was added as a 0.2% solution at 0.4% resin actives per dry paper while the dispersed stock slurry was mixing at 750 rpm. All handsheets were blotted dry between felt cloths. The wet sheets were dried and cured as specified in Table 1.

Wet tensile was measured from 1" x 4" strips after soaking in water for one hour and dry tensile was measured from unsoaked similar strips on an Instron Tester. Table 1 shows the increase in wet strength [(wet tensile/dry tensile) x 100] when the composition according to the invention was used to make paper sheets.

The data in Table 2 clearly shows that dry tensiles improve when the composition according to the invention is added to the stock prior to formation of the paper sheet.

Table 1<sup>1</sup>

Sample I.D.	% Wet Strength
Example 3	8.5
Example 5	14.6
Example 6	9.5
Example 7	12.0
Blank <sup>2</sup>	1.7
Fibrabon 33 <sup>3</sup>	16.3

<sup>1</sup> Handsheets dried at 105°C for 10 minutes and cured at 105°C for 30 minutes.

<sup>2</sup> No additives.

<sup>3</sup> Polyaminoamide-Epichlorohydrin Resin (Henkel Corporation).

Table 2<sup>1</sup>

Sample I.D.	% Dry Strength psi	% Increase Dry Tensile (over Blank)
Example 8	16.1	24.8
Fibrabon 33 <sup>2</sup>	15.0	16.3
Blank <sup>3</sup>	12.9	--

<sup>1</sup> Handsheets cured at 70°C for 16 hours at 50% relative humidity.

<sup>2</sup> Polyaminoamide-Epichlorohydrin Resin (Henkel Corporation).

<sup>3</sup> No additives.

WHAT IS CLAIMED IS:

1. A thermosetting, cationic wet-strength resin composition comprising the reaction product of a polyamine, a polyaminoamide or an alkylated polyaminoamide with a cross-linking agent selected from the group consisting of diepoxides, piperazine dichlorohydrin, methylene bis-acrylamide, chloroacetyl chloride and maleic anhydride wherein said cross-linking agent is present in said reaction product in an amount sufficient to provide a mole ratio with reactive nitrogen of the amine compound of at least about 0.375.
2. The wet-strength resin composition of claim 1 wherein said mole ratio is from about 0.375 to about 3.0.
3. The wet-strength resin composition of claim 1 wherein the diepoxide is selected from the group consisting of 5-ethyl-1,3-diglycidyl-5-methyl hydantoin, dimethylhydantoin diepoxide, pentamethylene hydantoin diepoxide, ethyl amyl diepoxide and 1,4-butane diepoxide.
4. The wet-strength resin composition of claim 1 wherein the polyamine is selected from the group consisting of polymers of ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, bis-hexamethylene triamine, polyethylenimine, polyallylamine, and polydiallylamine.



5. A method of preparing a wet-strength resin composition comprising reacting a polyamine, a polyaminoamide or an alkylated polyaminoamide with a cross-linking agent selected from the group consisting of a diepoxide compound, piperazine dichlorohydrin, methylene bis-acrylamide, chloroacetyl chloride and maleic anhydride wherein the mole ratio of said cross-linking agent to reactive nitrogen of said polyamine or polyaminoamide is at least about 0.375.

10 6. The method of claim 5 wherein the mixture contains dimethyl glutarate and dimethyl adipate.

7. The method of claim 5 wherein said polyamine is selected from the group consisting of polymers of ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, bis-hexamethylene triamine, polyethylenimine, polyallylamine, and polydiallylamine.

8. The method of claim 5 wherein said diepoxide compound is selected from the group consisting of 5-ethyl-1,3-diglycidyl-5-methyl hydantoin, dimethyl hydantoin diepoxide, pentamethylene hydantoin diepoxide, ethyl amyl diepoxide and 1,4-butane diepoxide.

9. The method of claim 5 comprising adding said cross-linking agent to a water-polyol-polyamine solution at

a rate sufficient to maintain the temperature of the solution in the range of from about 5°C to about 25°C and reacting the cross-linking agent and the solution at a temperature of no higher than about 100°C.

- 5           10. The method of claim 5 comprising adding said cross-linking agent to an aqueous solution of a polyaminoamide or alkylated polyaminoamide thereof at a rate sufficient to maintain the temperature of the solution from about 5°C to 50°C and reacting the cross-linking agent  
10           and solution at a temperature of from about 15°C to 100°C.

11. The method of claim 5 wherein the polyaminoamide is prepared by reacting a diacid, a diester or mixture thereof with an amine compound.

12. The method of claim 11 wherein the diacid is  
15           selected from the group consisting of glutaric acid, adipic acid and mixtures thereof.

13. The method of claim 11 wherein the diester is selected from the group consisting of dimethyl glutarate, dimethyl adipate and mixtures thereof.

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : C08L 63/00, 77/06, 97/02; C08K 03/20

US CL : 525/423; 528/422; 523/402

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/423; 528/422; 523/402; 162/164.3

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	US, A 4,145,247 (ELDIN ET AL.) 20 March 1979, Abstract, col. 2, lines 6-10, col. 3, lines 63-66, col. 4, lines 48-52, Claim 4.	1-3, 5, 8-10 ----- 1-13
X ----- Y	US, A, 4,143,188 (HUBER-NUESCH ET AL.) 06 March 1979, col. 3, line 52, col. 4, lines 1-25, col. 6, lines 45-68, col. 8, lines 33-47, and Claim 7.	1-3, 5, 8-10 ----- 1-13
X	US, A, 4,250,298 (LEHMANN ET AL.) 10 February 1981, col. 1, lines 37-41, col. 1, lines 57-61, col. 4, lines 1-36, col. 4, lines 48-51, col. 11, lines 47-53, col. 12, lines 30-36 and Examples Polyamine 1 to Polyamine 12.	1-3, 5-6, 8-13

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be part of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* "E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* "L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* "O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
* "P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

25 APRIL 1995

Date of mailing of the international search report

23 MAY 1995

 Name and mailing address of the ISA/US  
 Commissioner of Patents and Trademarks  
 Box PCT  
 Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

DONALD R. WILSON

Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)\*

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,189,142 (DEVORE ET AL.) 23 February 1993, col. 1, lines 41-55, col. 2, lines 54-62, and Examples 1-2.	1-3, 5-6, 8-13
X	US, A, 3,462,383 (LONGORIA III ET AL.) 19 August 1969, col. 1, lines 30-53, col. 2, lines 20-50 and Example 1.	1-2, 4-5, 7, 9-10
Y		1-13
Y	US, A, 3,640,909 (JONES ET AL.) 08 February 1972, Abstract, and col. 2, lines 10-37 and 51-62.	1-13
Y	US, A, 3,748,221 (STOCKMANN ET AL.) 24 July 1973, col. 4, lines 17-32).	1-13
X	US, A, 4,319,019 (LEHMANN ET AL.) 09 March 1982, col. 1, lines 6-37, col. 1, line 53 to col. 2, line 24, col. 3, line 41 to col. 5, line 27, col. 5, lines 36-64, col. 6, lines 8-12, and Example Polyamine 1.	1-13
X	US, A, 3,803,237 (LEDNICER ET AL.) 09 April 1974, col. 1, line 70 to col. 2, line 57, and col. 3, line 4-18.	1-2, 4-5, 7, 9-10

Form PCT/ISA/210 (continuation of second sheet)(July 1992)\*

**B. FIELDS SEARCHED**

Electronic data bases consulted (Name of data base and where practicable terms used):

APS

search terms: ?hydantoin(3A)?glycidyl, polyaminopolyamide#, polyamidopolyamine#, polyamine#,  
polyamino(w)polyamide#, polyamido(w)polyamine#, aminopolyamide#, wet strength resin#

' • , -

• • • •

—

— 11 —

100 50 0 0

1. *Phragmites australis* (Cav.) Trin. ex Steud.

2000年12月29日  
 2001年1月1日